Chapter 5
Grain Boundary Modeling

All structures tend to reach a minimum energy configuration; a perfect single crystal, for example, is the illustration of such configuration. However, the former structure with very low internal energy may not be suitable for all domains of application. Indeed, depending on the desired performance, the introduction of defects into a perfect microstructure can prove advantageous. Doped silicon plates and doped ceramics are good examples of the possible ameliorations resulting from the presence of defects in a material. Similarly to dopants, grain boundaries can lead to improved materials response. In general, grain boundaries provide barriers to the motion of dislocations within a grain – this in turns leads to a more pronounced hardening – and can also act as barrier to crack propagation, which can improve the materials’ ductility.

As mentioned in Chapter 2, the volume fraction of grain boundaries is significantly higher in NC materials than in coarse-grain materials. Recall that grain boundary volume fractions as high as 50% were reported in early work on the matter. Clearly, the response of NC materials is affected by the amount and type of grain boundaries composing its microstructure. In Chapter 2, it was also seen that, along a given direction, a grain boundary can exhibit a changing character. That is, some regions of a grain boundary can exhibit no organization of their atomic arrangements while other regions may be well defined. Disordered regions can be considered as amorphous regions which typically exhibit an elastic perfect plastic response. However, the response of ordered regions of grain boundaries is less well known. This chapter discusses only ordered grain boundaries, for much can be learned from them.

Grain boundary modeling, in terms of geometry, elastic stress field, and excess energy, has motivated a large body of research over the past century. Clearly, it is out of the scope of this chapter to review all studies related to grain boundaries. The objective here is to recall key results related to grain boundaries. In particular, a short background will be given prior to describing continuum mechanic–based models. While at first sight continuum models may appear as obsolete compared to numerical models, the complementarity of the two approaches will be demonstrated with applications.
5.1 Simple Grain Boundaries

Let A and B denote two separate crystal with similar structure. Upon joining crystal A and B, one creates a bicrystal containing a grain boundary. The geometry of the grain boundary does not depend only on the relative orientation of the two crystals. In general, a grain boundary has five macroscopic degrees of freedom and three microscopic degrees of freedom. Macroscopically, three degrees of freedom (e.g., rotations) are used to orient crystal B with respect to crystal A. Once the two crystals have been oriented, the plane defining the grain boundary must still be assigned. This choice consumes two degrees of freedom (rotations with respect to the two grains) [1]. In this case, there is no third degree of freedom assigned to the plane orientation since rotating a plane with respect to its normal does not affect the plane orientation. Microscopically, the three remaining degrees of freedom correspond to the translation vector of the two crystals composing the bicrystal.

It is easy to conceive that modeling of a general grain boundary – with its eight degrees of freedom assigned randomly – would be a gargantuan task. Instead, two types of grain boundaries have been subject to modeling efforts. These grain boundaries are referred to tilt and twist angle grain boundaries.

Let \( \mathbf{u} \) be the unit vector representing the axis of relative orientation of the two crystals. The orientation of crystal B with respect to crystal A can then be given by vector \( \mathbf{w} = \theta \mathbf{u} \). Here, \( \theta \) denotes the rotation angle. Each of the three components of \( \mathbf{w} \) represents one of the three degrees of freedom necessary to orient B with respect to A. The boundary orientation – the last two degrees of freedom – can be assigned with unit vector \( \mathbf{n} \) denoting the normal to the grain boundary plane. With the above geometrical consideration, twin and tilt grain boundaries can be defined. As given by Read [2] – who pioneered the area of grain boundary engineering – a tilt grain boundary is such that the axis of relative orientation of the crystals, \( \mathbf{u} \), lies in the grain boundary plane. In other words, \( \mathbf{u} \) is perpendicular to \( \mathbf{n} \). On the contrary, a twist grain boundary is such that \( \mathbf{u} = \mathbf{n} \). In other words, the axis of relative orientation of the crystals is perpendicular to the grain boundary plane. A schematic of the simplest tilt grain boundary is given in Fig. 5.1(a). More tortuous geometries

![Fig. 5.1 (a) Simple tilt grain boundary, (b) simple twist grain boundary](image-url)
could obviously be designed. Crystal A appears in red while crystal B appears in blue, and the grain boundary is defined as the region of intersection of both crystals (in dark red). The grain boundary plane is defined with vectors $\mathbf{u}$ and $\mathbf{v}$. Fig 5.1(b) shows a schematic of a simple twist grain boundary.

5.2 Energy Measures and Numerical Predictions

As expected, the energy of a given grain boundary is dependent on each of its degrees of freedom. In the case of tilt and twist grain boundaries, the interphase energy is thus dependent on the misorientation angle between the two crystals and on the grain boundary plane.

Grain boundary free energies can be measured experimentally via use of Herring’s formula, which was originally derived from a variational approach (e.g., virtual displacements). Consider the junction of three crystals, as shown in Fig. 5.2, and let OA, OB, and OC represent respectively the interface between crystal 1 and 2, crystal 2 and 3, and crystal 3 and 1, respectively. Also let $\gamma_1$, $\gamma_2$, $\gamma_3$, and $\phi_1$, $\phi_2$, $\phi_3$ denote the corresponding free energies and the angle formed by the interfaces, respectively. Let us note here that for the sake of simplicity the twists’ contributions are not accounted for. The equilibrium configuration of the tricrystal is then given by [3]:

![Fig. 5.2 Junction of three grain boundaries](image)
\[
\frac{\gamma_1}{\sin \phi_1} = \frac{\gamma_2}{\sin \phi_2} = \frac{\gamma_3}{\sin \phi_3}
\]  

(5.1)

Using Herring’s formula, Gjostein and Rhines [4] systematically measured the interface free energy of simple tilt and twist grain boundaries with misorientation angles ranging from \(\sim 0\) to \(\sim 70^\circ\) in the case of copper. Figure 5.3 presents the measured data in the case of \(\langle 001\rangle\) pure tilt boundaries. The dashed line does not have any physical significance and simply serves as a guideline.

From Fig. 5.3, it can be seen that the energy of a simple tilt grain boundary increases with increasing misorientation angle, with a maximum at \(43^\circ\) after which the energy decreases. A similar trend was obtained in the case of pure twist grain boundaries. The experimental measures presented in the above do not exhibit the presence of “metastable” misorientations which would translate by the presence of cusps – additionally to the \(\theta = 0\) cusp – in Fig. 5.3. However, the existence of such metastable configurations was clearly shown in several experiments. For this purpose, Chan and Baluffi [5] used the crystallite rotation method on Au \([001]\) twist grain boundaries. It consists of first sintering small crystallites (\(\sim 80\) nm in diameter) onto a specimen at predetermined twist orientations and then subjecting the specimen to an anneal in situ so as to observe grain rotation towards relaxed configurations. It was found that all lattice oriented with \(\theta < 34^\circ\) tended to reorient towards \(\theta = 0\), all lattice initially in the \(35 \leq \theta \leq 40\) range reoriented towards \(\theta = 36.9^\circ\), and all crystallites orientated with \(\theta < 40^\circ\) reoriented towards \(\theta = 45^\circ\). From these anneal experiments it can be concluded that these particular twist orientation (e.g., \(\theta = 0, 36.9\) and \(45\)) appear more energetically favorable than other random orientations. Yet, these energy cusps were not rigorously found in measures shown in the above (Fig. 5.3).

![Fig. 5.3 Energy evolution with misorientation angle for copper pure tilt \(\langle 001\rangle\) grain boundaries. Experimental data from Gjostein and Rhines [4]](image-url)
On the other hand, molecular statics simulations were used to assess of the presence of energy cusps. These simulations were part of an extensive molecular based set of simulations by D. Wolf [6, 7]. Figure 5.4(a) and (b) presents the predictions of the evolution of symmetric tilt grain boundary free energy with misorientation angles for boundary planes perpendicular to the \( <001> \) and \( <112> \) orientations for Cu, respectively. Crosses refer to calculated date while lines serve as a guide to the eye. In order to overcome limitations related to the use of a particular potential, the author used both the Lennard Jones (LJ) potential and the embedded atom method (EAM) potential (which, as was discussed in Chapter 4, is more adequate to model FCC structures). In the case of the \( <001> \) symmetric tilt grain boundary, the presence of energy cusps – corresponding to misorientations from which the energy increases at an infinite rate as the misorientation angle is slightly changed – can be observed at the \( (310) \) 36.87° and \( (210) \) 53.13° misorientations. Similarly, energy cusps are predicted in the case of \( <112> \) symmetric tilt grain boundaries.

The existence and particular orientations corresponding to energy cusps both in symmetric tilt and twist grain boundaries has stimulated a large body of research aiming at understanding the correlation between grain boundary energy and it structure.

5.3 Structure Energy Correlation

Figure 5.1 clearly does not show the details of the atomic structure of the grain boundary nor does it explain the particular energy dependence on misorientation angles. Based on molecular simulations which revealed particular atomic arrangements within both tilt and twist grain boundaries, to be presented in what follows, several models resulting from physical considerations were introduced to easily describe and predict important atomic features of grain boundaries.
Prior to introducing these models let us discuss important geometrical and physical features of grain boundaries. First, grain boundaries can typically be sorted as low angle grain boundaries and large angle grain boundaries. Low-angle grain boundaries exhibit well-organized structures characterized by the discernible presence of dislocation arrays. Read and Shockley [8] first introduced a two-dimensional continuum model based on the dislocation arrangements allowing the prediction of the evolution of low angle grain boundaries as a function of misorientation angle [2]. This model will be presented next. Typically, the distinction between low- and large-angle grain boundaries is established on the following basis. As one fictitiously increases the misorientation angle of a given low-angle grain boundary, the dislocation density with the grain boundary increases (according to Frank formula). In the limit case, the number of dislocations composing the grain boundary will be such that the core of each dislocation will intersect. This limit case defines the onset of the domain of misorientation of large-angle grain boundaries. Typical values range between 20° and 25° of misorientation. With the argument in the above, one expects significant structural differences between low- and large-angle grain boundaries. However, this does not mean that large-angle grain boundaries necessarily lack structure. The following two subsections will present structure energy correlation models for both low-angle grain boundaries and large-angle grain boundaries.

In terms of statistical distribution of low- and large-angle grain boundaries, it was shown in work by Warrington and Boon [9] that, in polycrystals with random grain boundary distribution, the probability of low-angle grain boundaries should equal 0.000825. Deviation from this number would indicate that the grain boundary distribution is not given by a random distribution. In connection with Chapters 1 and 2, it can clearly be seen that the grain boundary distribution in NC materials is clearly not random.

5.3.1 Low-Angle Grain Boundaries: Dislocation Model

As mentioned above, low-angle grain boundaries are often assimilated, and several experimental studies concur with this conceptualization, as particular arrangements of dislocations. Let us clarify this concept by considering, as in the original work of Read [2] and Read Shockley [8], the formation of a low-angle tilt grain boundary. Read proposed the following representation of a low-angle grain boundary: in Fig. 5.5(a) two crystals (red and blue) are not yet connected by a grain boundary, upon creating the low-angle grain boundary (Fig. 5.5(b)), dislocations are present geometrically to ensure the degree of misorientation between the two crystals. In our case, disregarding other dislocation pairs which may be present in an actual grain boundary and would disappear after an anneal process, the minimum set of dislocations present in the grain boundary is an array of edge dislocation all parallel to the [001] axis.
The misfit between the two crystals is accommodated by both atomic misfit and elastic deformations. Note that in order to reduce the elastic energy within the grain boundary, the [100] planes of crystal A and B end at alternating intervals.

In the case of a simple symmetric tilt-angle grain boundary, the mean dislocation spacing $D$ is given by Frank’s formula, which is obtained with the following simple geometrical consideration: if $D$ represents the average spacing between dislocations, each with Burgers vector $b$ leading to $b/2$ net displacement on each side of the grain boundary median plane (parallel to (001)), then recalling the misorientation angle on each side of the median plane is $\theta/2$ (see Fig. 5.1(a)), one obtains:

$$D = \frac{b}{2 \sin(\theta/2)} \quad (5.2)$$

Rigorous extensions of this simple law in the case of grain boundaries containing two or more different dislocation types can be found in Hirth and Lothe [10]. From this structural representation of low-angle grain boundaries, Read and Shockley developed a model entirely based on dislocation theory and predicting the energy vs. misorientation angle. While the model was limited to a two-dimensional representation, it could very well be extended to be fully three dimensional.

Read and Shockley and later Read proposed two derivations of their model, the first one being based solely on mathematical considerations while the second one is based on a more physical reasoning. For the sake of simplicity, only the intuitive derivation will be shown in detail and the mathematical derivation will only be briefly summarized.
First Proof: Physical Considerations

Let us consider the case of a simple tilt-grain boundary, as shown in Fig. 5.5(b). This grain boundary is composed of an array of edge dislocations. An equivalent representation of this simple grain boundary is presented in Fig. 5.6(a), where the grain boundary is divided in strips of length $D$—which in the small angle approximation is given by $D \sim \theta/2$—, the average dislocation spacing, positioned such that each strip, of infinite width, contains an edge dislocation positioned in its center.

The energy of a given strip is the sum of three contributions: the core energy and the edge dislocation, encompassed in the circle of radius $r_0$; the elastic deformation energy of the dislocation, which is encompassed in the circular area in between $r_0$ and $R$, proportional to $D$ and which value will not affect the model’s prediction as long as $R < D$; and the remaining energy of the strip. Let us name these terms, by order of citation, $E_c$, $E_{el}$, and $E_{rem}$. Therefore, the free energy of a given strip of grain boundary is given by:

$$E_{el}^{GB} = E_c + E_{el} + E_{rem} \quad (5.3)$$

Let us now decrease the misorientation angle by an amount $-d\theta$ (see Fig. 5.6 (b)). Then using Frank’s formula in the above, the following relations are obtained:

$$-\frac{d\theta}{\theta} = \frac{dD}{D} = \frac{dR}{R} \quad (5.4)$$

Following the change in misorientation, the grain boundary energy will change by an amount $dE_{el}^{GB}$ which will be the sum of the energy changes of each term in equation. The core energy is not expected to change significantly. Similarly, it can be shown that the term $E_{rem}$ will not change when $\theta$ is changed. Indeed, as
can be seen in Fig. 5.6(b), the area represented by $E_{rem}$ increases with $D^2$ and the energy density varies as $1/D^2$.

In view of the argument above, the elementary change in the grain boundary energy following an elementary change in misorientation angle is given by the change in the elastic deformation energy of the dislocation. Formally, this is given by the energy in the ring encompassed in the radii $R$ and $R + dR$. In linear elasticity, $dE_{el}^{gb}$ corresponds to the work done by the dislocation on a fictitious cut of the ring, and one readily obtains:

$$dE_{el}^{gb} = \frac{1}{2} \tau dR \cdot b \quad (5.5)$$

Here $\tau$ denotes the shear stress on the cut of the ring and is given by $\tau \sim \frac{\sigma_b}{R}$. For further details, consult Hirth and Lothe and Read. Using the above relation, Equation (5.4) and integrating the result, one obtains the following expression of energy of a low-angle grain boundary.

$$E_{el}^{gb} = E_0(A - \ln \theta) \quad (5.6)$$

$E_0 \theta A$ is a constant energy per dislocation – including the energy of misfit in the core region – which is proportional to the density (i.e., to $1/D$). $-E_0 \theta \ln \theta$ is a term directly dependent on the elastic energy of a dislocation.

\textit{Second Proof: Mathematical Considerations}

In Read and Shockley’s original work, a more complex proof of relation (5.6) was given in the case of a simple grain boundary making an arbitrary angle $\phi$ about the common cube axis of the grain. In other words, a second degree of freedom is added and it corresponds to the orientation of the grain boundary plane. As mentioned above, such arbitrary grain boundary can be described by a multiple array of two different types of dislocations. Let us now summarize the methodology used to derive Equation (5.6).

- First, recall that the grain boundary energy can be written as the sum of a core part, inelastic by essence, and an elastic energy part. Rigorously, the core energy can be obtained by molecular simulations. Fortunately, in the case of low-angle grain boundaries, closed-form solutions can be found analytically.
- A longitudinal (x-axis) and a vertical axis (y-axis) is assigned to the grain boundary as well as corresponding dislocation densities (Frank’s rule). The latter are calculated by assuming that lattices’ planes are equivalent to dislocation flux lines.
- Choosing any “y” dislocation, the corresponding work term, which represents the elastic energy of such dislocation, can be calculated by considering the effect of all other “x” and “y” dislocations on its slip system. Similarly to Equation (5.5), the work terms are equal to half the lattice constant multiplied by the integral of the shear stress on the slip system. The energy
engendered by the “x” dislocations on the “y” dislocation is supposed not to depend on the position of the “y” dislocation and on the set of “x” considered. The same procedure is performed for an “x” dislocation.

- Finally, the interface energy per unit length is the sum, on the two types of slip systems (corresponding to the “x” and “y” dislocations), of the energy of a slip system multiplied by the number of slip systems. Although each term is diverging, the sum of the two terms converges. After some algebra one obtains equation (5.6).

In the case of this two degree of freedom grain boundary, the terms $E_0$ and $A$ are given by:

$$E_0 = \frac{Ga}{4\pi(1-\nu)} (\cos \phi - \sin \phi)$$ \hspace{1cm} (5.7)

and

$$A = A_0 - \sin 2\phi \left(\frac{\sin \phi \ln(\sin \phi) + \cos \phi \ln(\cos \phi)}{\sin \phi + \cos \phi}\right)$$ \hspace{1cm} (5.8)

where

$$A_0 = \ln\left(\frac{a}{2\pi r_0}\right)$$ \hspace{1cm} (5.9)

$G$, $\varphi$, $a$ and $\nu$ represent the shear modulus, the orientation of the grain boundary, the inverse of the plane flux density, and Poisson’s coefficient, respectively. $r_0$ is the lower bound used for the integration of the shear stress. This bound represents the smallest distance at which the material is elastically deformed.

The model above was applied to pure symmetric tilt grain boundaries in copper. Figure 5.7 presents a comparison between experimental data (dots) and the mode predictions (line). The model parameters $E_0$ and $A$ were chosen to obtain a best fit of the low-angle grain boundary region. It was shown elsewhere that these parameters should be changed to obtain a better fit for larger grain boundary misorientations (e.g., $\theta > \sim 6^\circ$). Regardless of the set of parameters chosen, the grain boundary dislocation model leads to adequate predictions only at low grain boundary misorientations.

### 5.3.2 Large-Angle Grain Boundaries

In order to circumvent the limitations of the grain boundary dislocation model, several models were developed to correlate the grain boundary energy with its macroscopic degrees of freedom (recall here that we focus primarily on pure tilt and twist grain boundaries). One of the objectives of these models also resides in
providing a rationale behind the presence of energy cusps shown in Fig. 5.4. In this section, the coincident site lattice model will be recalled as well as the structural unit model and the disclination model.

5.3.2.1 CSL Model

The first of these models, referred to as the coincident site lattice (CSL) model, fathered by Bollman [11], introduces a measure of fit/misfit between the two crystals with their respective lattice. This geometrical model has been widely accepted in the community and is now often used to quickly describe the grain boundary structure. This model does not allow quantitative evaluations of grain boundary energies but presents a first explanation for the presence of metastable grain boundaries, identified by the presence of cusps. The argument here is that lower-energy grain boundaries are composed of a structure in which a “best-fit” of the two interpenetrating lattices of crystal A and B is obtained.

In the CSL model, the atomic arrangement within a given grain boundary is considered to result from the rigid junction of the two bodies followed by relaxation to improve lattice matching. The match of the two lattices at the median plane of the grain boundary is formally given by the CSL content. The CSL content, which describes the frequency of atoms positioned such that they are located in the continuity of both lattices from crystal A and B, is quantified with \( \Sigma \). A coincident site is simply an atom in the grain boundary region which is in perfect continuity of both lattice A and B. This atom is a region of perfect match and is necessarily unstrained. Therefore, it is expected to be at a lower
energy level. Due to the periodicity of the lattice, if one coincident site exists then an infinity of similar points also exist, which leads to a coincident site lattice.

$\Sigma$ is given by the ratio of the volumes of the primitive unit cells of the CSL and the original crystal lattice. The lower $\Sigma$, the higher CSL content, and the better the match. In the BCC and FCC systems, $\Sigma = 3$ corresponds to a twin boundary. Clearly $\Sigma = 1$ corresponds to the perfect lattice case. To illustrate the evaluation of the CSL content, let us consider the following case of a $\Sigma = 5$ grain boundary presented in Fig. 5.8. Let us superimpose the lattices of crystal A and of crystal B, in red and blue, respectively. Crystal B is rotated by an arbitrary angle $\theta$. A local frame is attached to each crystal. Clearly it can be seen that, with the given misorientation of the two crystals, several coincident sites can be found. Such points can be found at the origin of the blue and red frames and can also be found at the blue and red circles. The CSL content can be calculated in the frames of both crystal A and of crystal B. In the frame associated with crystal A (red frame), $\Sigma'$ is given by the area of a unit cell of the CSL; this area is delimited by the x-axis and the vector relating two coincident sites (bold red vectors). One obtains $\Sigma' = 3^2 + 1^2 = 10$. Performing the same operation in the frame associated with the blue frame, one obtains $\Sigma = 2^2 + 1^2 = 5$. Bollmann introduced the following rule in calculating $\Sigma$: if $\Sigma$ is even then $\Sigma \leftarrow \frac{\Sigma'}{2}$, otherwise $\Sigma \leftarrow \Sigma$.

Upon rotating the two crystals A and B about the [001] direction, it can clearly be seen that all possible matching patterns are described in the range

![Fig. 5.8 Geometry of the coincident site lattice model](image)

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0 < θ < 45. Therefore, in referring to a grain boundary by use of the CSL notation, one cannot solely mention the rotation axis and the CSL content. Either the misorientation angle or the grain boundary plane must be specified to avoid confusion. For example, let us consider the case of symmetric tilt grain boundaries rotated about [001]. In this case, both 36.87° and 53.13° misorientation correspond to a Σ = 5 grain boundary. As shown in Fig. 5.5 there seems to be a correspondence between CSL boundaries and energy cusps. Indeed, it can be seen that in that molecular simulations predict energy cusps corresponding to both the Σ5 36.87° and 53.13° grain boundaries. The concept of the O-lattice will present a rationale for such correspondence.

Introduction to the O Lattice

Geometry

Clearly, the CSL model is discontinuous with respect to θ. In other words, not all grain boundaries form a coincident site lattice. Also, a limitation inherent to the discontinuity of the CSL model stems from the fact that, as a coincident site is slightly moved out of its best fit position, the CSL model breaks down. In order to overcome such limitation, the CSL model was generalized, which lead to the concept of the O-lattice. The objective here is simply to introduce such a concept, for more details the reader is referred to Bollmann’s book [11] and to the review by Balluffi et al. [12]

Prior to introducing the mathematics behind the O-lattice, let us present the idea behind it. A crystal lattice is composed of lattice point and also of “voids” present within each elementary cell of the crystal. An O-lattice point is simply a point of match between the two crystals. Here, the word point is meant in its general sense – it can either be a lattice point or a point where no atom is located.

Mathematically, the position of O-points engenders the existence of an O-lattice and can be assessed with the following reasoning. First, let the matrix \( R \) denote the transformation from lattice A to lattice B. Then any geometrical point of crystal A, which is given in term of its internal coordinates within a crystal cell and with the coordinates of the cell, is related to one of crystal B as follows:

\[
X^B = R \cdot X^A \tag{5.10}
\]

Any point of the same class as \( X^A \) (i.e., having similar internal coordinates within a cell but different cell coordinate) can be related to \( X^A \) via a simple lattice translation given by vector \( t^A \):

\[
X^A' = X^A + t^A \tag{5.11}
\]

An O-point, denoted \( X^O \) must necessarily respect the conditions given by Equations (5.10) and (5.11). Therefore it is given by:

\[
(I - R^{-1})X^O = t^A \tag{5.12}
\]
With the relation above one can find the coordinates of the O-lattice. It can be seen that a coincident site is a particular O-point located at the corner of a cell. The solution of Equation (5.12) is left as an exercise for it is treated in great detail by Bollman [11]. However, let us note that the solution of Equation (5.12) for all possible cases shows that O-points are bounded in cells whose boundaries, defined by grain boundary dislocations, correspond to regions of worst fit between the lattices.

Significance

As mentioned earlier, the concepts of the coincident site lattice and its generalization (e.g., the O-lattice) were initially introduced to predict energetically favorable grain boundary orientation without the actual knowledge of the grain boundary energy. O-points define best matching points between the lattices defining the grain boundary. Therefore, one expects that the better the match, the lower the grain boundary energy. The question of finding minimum energy grain boundaries is thus equivalent to finding the periodicity of O-lattice points with the idea that smaller periods lead to more favorable grain boundaries. Two cases must then be considered.

First, when the O-lattice cells are much larger than the crystal lattice cell, then one can imagine that grain boundary relaxation is initiated at O-points and stops at cell walls. In that case, the periodicity of O-points is less relevant. Second, in the case where the O-lattice cells are of comparable size to that of the crystal lattice, then Bollman introduces the concept of pattern elements which are defined as subpattern of the grain boundary. The idea is that if a grain boundary is periodic it must be composed of a limited number of pattern elements. This idea is important because, as will be presented in an upcoming section, it is in direct connection with structural unit models. The number of pattern elements is equal to the number of different O-points with different internal coordinates.

Following the procedure introduced by Bollmann, the periodicity of the O-points can be calculated. Minimum energy grain boundaries then correspond to lower periods. In the O-lattice model, the presence of cusps in the energy vs. misorientation profiles result from the fact that a grain boundary whose misorientation is in the neighborhood of a minimum energy misorientation grain boundary will keep minimum energy periodicity of the grain boundary pattern, in order to remain in a relatively low energy state, with the presence of grain boundary dislocations. The presence of such dislocations is similar to the construction shown in Fig. 5.5 for low-angle grain boundaries. The Burgers vector of such grain boundary dislocations can be calculated via geometric arguments similar to that presented in Equations (5.10), (5.11), and (5.12). Finally, the presence of such grain boundary dislocation has been reported in several experimental studies [13].

5.3.2.2 Structural Units Models

Regardless of their agreement (or disagreement) with experimental measures, the O-lattice theory and the CSL model do not allow the evaluation of the
relative grain boundary energy as a function of misorientation angle (in the case of pure tilt and twist grain boundaries). Nonetheless, these models bring out two interesting ideas.

First, grain boundaries exhibiting periodicity should be composed of a finite number of subpatterns. As will be seen in this section, molecular statics simulations will confirm this first point.

Second, departure from favorable misorientation is expected to be coupled with the presence of grain boundary dislocations (referred to as secondary dislocations). This second point was already discussed in Read and Shockley’s original model. Indeed, in the dislocation model, the dislocation spacing is supposed uniform and the distance between dislocation is assumed to be a multiple of the distance between atomic planes. When this is not the case, additional dislocations are present within the grain boundary, as predicted by the O-lattice theory, the additional energy arising from the presence of such dislocations follows an equation similar to (5.6) where the misorientation angle is replaced by its deviation from an orientation considered in the dislocation model. In that case, energy cusps are expected when the spacing between the added dislocations is a multiple of the atomic planes spacing.

The structural unit model [14–16] is based on the two ideas presented above and is subsequently to be considered as an extension of the Read and Shockley dislocation model. The geometry of tilt boundaries was first investigated via molecular statics simulations on high $\Sigma$ tilt grain boundaries. These simulations lead to the following postulates:

- Within a misorientation range, all tilt boundaries, with same median plane, are composed of a mixture of two structural patterns referred to as structural units.
- The grain boundaries limiting the misorientations range are composed of either a single type of fundamental structural unit or of multiple fundamental structural units. In that case, the delimiting grain boundary is referred to as multiple unit reference structure.
- Within two limiting grain boundaries are two structural units of the limiting grain boundary. The sequence of a structural unit is such that the minority units have the maximum spacing possible.

For example, it was shown that, in FCC metals, [001] symmetric tilt boundaries have the following delimiting ranges with following fundamental structural units (see Table 5.1):

<table>
<thead>
<tr>
<th>Table 5.1</th>
<th>Delimiting grain boundaries for symmetric tilt [001] orientations</th>
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<tbody>
<tr>
<td>Range</td>
<td>Delimiting fundamental structural unit and corresponding $\Sigma$ notation</td>
</tr>
<tr>
<td>$0^\circ \rightarrow 36.87^\circ$</td>
<td>D, $\Sigma 1(110)$</td>
</tr>
<tr>
<td>$36.87^\circ \rightarrow 53.13^\circ$</td>
<td>C, $\Sigma 5(310)$</td>
</tr>
<tr>
<td>$53.13^\circ \rightarrow 90^\circ$</td>
<td>B or $B'$, $\Sigma 5(210)$</td>
</tr>
<tr>
<td></td>
<td>A, $\Sigma 1(100)$</td>
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</table>
It was shown that both $\Sigma 5$ grain boundaries have two metastable states B and $B'$ and C and $C'$. For the sake of simplicity these will not be recalled here. For the sake of illustration the structure of a $\Sigma 5(210) 36.87^\circ$ symmetric tilt boundary and of a $\Sigma 13(510) 67.38^\circ$ are shown in Fig. 5.9 [17]. In the following chapter, it will be shown that the presence of particular structural units (E structural units) can significantly affect the response of NC materials.

With the structural unit representation of grain boundaries and Read and Shockley’s dislocation model, grain boundary energies as a function of misorientation angle can be predicted. Similarly to the dislocation model, the grain boundary energy can be written as the sum of a core energy term and an elastic energy term. The former will be calculated via the use of both molecular statics, giving the energy of particular structural units, and the structural unit model. The latter is the result of the presence of additional structural dislocations in the minority unit, which provides the misorientation away from the delimiting grain boundary. Therefore, the elastic contribution to the energy is given by Equation (5.6). The total grain boundary energy (per unit area) is written as follows.

$$E_{GB} = E_{el}^{co} + E_{GB}^{co}$$ (5.13)

The calculation of core contribution, $E_{GB}^{co}$, is obtained via use of the structural unit model. Let us consider the case of a grain boundary composed of $n$ structural units of type C and $m$ structural units of type D. Also let $n > m$ such that C is the majority unit. In the case where $n = 5$ and $m = 2$, the grain boundary would then be of the form shown in Fig. 5.10.

The core energy of the grain boundary is then given by the sum of the contributions of segment CC and of segments CD (see Fig. 5.10). Let $d_C$, $d_{CD}$ and $E_C^{co}$, $E_D^{co}$ denote the distance between two C units, the distance between a C unit and a D unit, and their respective energies with unit area. The core energy of the grain boundary is thus given by:

$$E_{GB}^{co} = \frac{[(n - m)d_CE_C^{co} + md_{CD}E_D^{co}]}{mD}$$ (5.14)

\[\text{Fig. 5.9 Structures of (a) } \Sigma 5(310) 36.87^\circ, \text{ and (b) of a } \Sigma 13(510) 67.38^\circ \text{ symmetric tilt boundary. Images extracted from [17, 18]}\]
Recall that $D$ denotes the average spacing between grain boundary dislocation and, therefore, with the previously mentioned argument, the average distance between minority structural units. Therefore, one obtains the following relation between $D$, $d_C$ and $d_{CD}$:

$$mD = (n - m)d_C + md_{CD}$$  \hspace{1cm} (5.15)

With (5.13), (5.14), (5.15), and Frank’s formula the grain boundary core energy can be written as follows:

$$E_{co}^{GB} = E_{co}^{C} + d_{CD}(E_{co}^{CD} - E_{co}^{C}) \frac{\theta}{b}$$  \hspace{1cm} (5.16)

The structural unit model has the same limitation as the grain boundary dislocation model in the sense that the core radius is unknown and must then be calculated to obtain a best fit. Figure 5.11 presents the model prediction (line),
for which the core radius and Burgers vector are recalculated for various misorientation ranges and molecular statics simulations predictions (dots). The model allows an excellent fit of the atomistic predictions. Particularly, energy cusps are predicted in agreement with molecular simulations.

### 5.3.2.3 Disclination Models

Let us now introduce a third type of model based on the concept of disclinations. This model was first introduced by J.C.M. Li [19] and then applied by Shih and Li [20] to predict the energy dependence on misorientation in between energy cusps. The disclination model relies on the following idea: since grain boundaries are regions of intersections of two crystals with different rotational orientations, instead of describing their geometry with an assembly of linear defects, namely dislocation, a one-dimensional rotational defect, referred to as Volterra dislocation or as disclination, is used.

In what follows, the concept of disclination and disclination dipoles will first be briefly introduced, then the disclination model will be introduced.

**Introduction to Disclination and Disclination Dipoles**

Similarly to a dislocation, a disclination is a linear defect [21]. However, instead of translating the lattice in a manner similar to a dislocation, it leads to a lattice rotation. In other words, disclinations can be perceived as rotational defects bounding the surface of a cut to a continuum medium. This is illustrated in Fig. 5.12(a) and (b) presenting a wedge disclination. If $u$ denotes the displacement between the two undeformed faces of the cut, then it is related to the disclination’s strength –denoted with its Frank vector $w$ which is equivalent to Burgers vector for dislocations – via the following relation:

$$u = (r - r_0) \times w$$

(5.17)

Here, $r$ and $r_0$ denote the core radius and the distance between the rotation axis and the longitudinal axis of the cylinder. For ease of comprehension, one can consider that a disclination corresponds to the addition or to the subtraction of matter at the surface of a cut. A disclination is said to be positive if matter is subtracted to the medium and negative otherwise. Also, similarly to dislocations which can have either an edge or a screw character, a disclination can have a wedge (Fig. 5.12(a)) or a twist character. In that case, its Frank vector is perpendicular to the cylinder’s radius. In what follows we are only interested in wedge disclinations.

Geometrically, it can be seen that a wedge disclination is equivalent to a wall of edge dislocations. Indeed as shown in Fig. 5.12(b) a wedge disclination of strength $w$ leads to the same displacements as a wall of edge dislocations, with Burgers vector denoted $b'$, equally spaced such that the distance between two dislocations is related to the disclinations’ strength as follows:
As mentioned by Li, this representation falls apart when \( w \) is a symmetry operation. Note that disclination models are equivalent to dislocations arrangements solely in terms of stress field or strain field (but not both).

The geometrical equivalent representation between disclinations and dislocation walls suggests that grain boundaries could be equivalently represented by a disclination model. Moreover, as extensively presented by Romanov [21] any disclination can be equivalently represented by an arrangement of dislocations. Conversely, for any dislocation, an equivalent disclination arrangement can be found. For further detail the reader is referred to Romanov [21] and Romanov and Vladimirov [22].

As will be seen later, among the many equivalent dislocation/disclination representations, the equivalent representation of interest here is that of an edge dislocation. It can be shown that an edge dislocation can be equivalently represented as a single line two-rotation axis dipole; that is, two parallel disclinations of same strength but opposite signs separated by a small distance. Let us now see the advantage of disclination arrangements.

The stress field of a wedge disclination can be obtained without too much strain via elasticity theory since the displacements are known. The derivation

\[
\tan\left(\frac{w}{2}\right) = \frac{b'}{2h'}
\]  

(5.18)
becomes more difficult in the case of twist disclinations. Huang and Mura [23] obtained the following expression of the stress field, in units of $\mu w/(2\pi(1 - \nu))$, of a wedge disclination (only the nonvanishing terms are presented):

$$
\sigma_{xx} = \frac{1}{2} \ln \left( \frac{R^2}{x^2 + y^2} \right) - \frac{y^2}{x^2 + y^2}, \quad \sigma_{yy} = \frac{1}{2} \ln \left( \frac{R^2}{x^2 + y^2} \right) - \frac{x^2}{x^2 + y^2} \quad (5.19)
$$

$$
\sigma_{zz} = \nu \left[ \ln \left( \frac{R^2}{x^2 + y^2} \right) - 1 \right], \quad \sigma_{xy} = \frac{xy}{x^2 + y^2} \quad (5.20)
$$

The expressions in the above are written in the case of isotropic elasticity where $\nu$ is the Poisson ratio and $\mu$ is the shear modulus. Also, $w$ is parallel to the $z$-axis, $R$ denotes the outer radius of the medium considered, and the position vector is given by the $x$ and $y$ coordinates. Clearly, it can be seen that the stress field ($\sigma_{xx}$, for example) rapidly diverges as $x^2 + y^2$ approaches $R$. However, it can be easily shown that the energy of the wedge dislocation remains bounded. Nonetheless, the diverging stress field of a single disclination may be considered as an argument preventing the use of disclination theory.

Consider now a single line two-rotation axis dipole where the disclinations are separated by a small distance $\delta y$. Then, the stress field of disclination dipole can be estimated with a Taylor’s expansion (only the first term is kept). Therefore, taking the derivative of (5.19) and (5.20) with respect to $y$, one obtains the following expression of the stress field of the dipole considered, in units of $\delta y \cdot \mu w/(2\pi(1 - \nu))$:

$$
\sigma_{xx} = - \frac{y(y^2 + 3x^2)}{(x^2 + y^2)^2}, \quad \sigma_{yy} = \frac{x(x^2 - y^2)}{(x^2 + y^2)^2} \quad (5.21)
$$

$$
\sigma_{zz} = - \frac{2\nu y}{(x^2 + y^2)^2}, \quad \sigma_{xy} = \frac{x(x^2 - y^2)}{(x^2 + y^2)^2} \quad (5.22)
$$

In the expression above, one recognizes the expression of the stress field of an edge dislocation with Burgers vector $w \delta y$, which shows the equivalence between the disclination dipole considered in the above and an edge dislocation. More importantly, it can be seen that, contrary to the stress field of a disclination, the stress field of a screened disclination (e.g., disclination dipole) is not diverging. Therefore, it would be safe to assume that grain boundaries in general, and at least low-angle grain boundaries, could be modeled with use of disclination dipoles.
Relationship to Excess Energy Between Cusps

The disclination grain boundary model, which predicts the evolution of energy vs. misorientation in between energy cusps, is based on the following geometrical representation of grain boundaries, which is somewhat similar to the subpattern and structural unit model. In between two energy cusps, with misorientations $\theta_1$ and $\theta_2$, the grain boundary is represented as an alternate assembly of single line double rotation axis dipoles of strength $w_1 = \theta_1$ and $w_2 = \theta_2$. If $2L_1$ and $2L_2$ denote the separation distances between two $w_1$ and two $w_2$ dipoles, respectively, then for a given misorientation $\theta$ such that $\theta_1 < \theta < \theta_2$ one has the following relation:

$$\theta = \frac{L_1 w_1 + L_2 w_2}{L_1 + L_2} \quad (5.23)$$

This subpatterning of the grain boundary clearly differs from the structural unit model. Indeed, the sequence of disclination dipoles is not given by the minority unit rule presented in the above. Also, in the present model each cusp orientation necessarily represents a delimiting grain boundary (e.g., $\theta_1$ or $\theta_2$). Since all dipoles parallel Frank’s vector, the sequence of alternating dipoles $w_1$ and $w_2$ is equivalent elastically to an alternate sequence of dipoles $\pm \Delta w = \pm (w_1 - w_2)$ with separation $H = 2L_1 + 2L_2$.

The excess energy between two energy cusps then resumes to the energy of a dipole wall. Using an edge wall dislocation representation of the dislocation dipoles, the excess energy between cusps is then the sum of the energy of edge dislocation walls of length $H$. After some algebra, one obtains:

$$E = \frac{\mu (\Delta w)^2}{8\pi(1-\nu)4\pi^2} f(\lambda_1) \quad (5.24)$$

with

$$f(\lambda) = -16 \int_0^\lambda (\lambda - \psi) \ln(2\sin \psi) d\psi \quad \text{And} \quad \lambda_1 = \frac{2\pi L_1}{H} \quad (5.25)$$

Typically, this model leads to fairly good agreement with experimental data. While it is of relatively easy use, for there is only one parameter that needs to be determined and no simulations at the atomistic scale are necessary, unlike the disclination model presented above, a priori knowledge of energy misorientation cusps is required. Nonetheless, it will be seen in next section that disclination-inspired grain boundary models have the great advantage of allowing modeling of grain boundary dislocation emission.
5.4 Applications

So far, several models were introduced to describe the structure of simple grain boundaries and to predict their corresponding energy. Let us now show how these models combined with purely numerical simulations (molecular statics and dynamics) can be used to predict the occurrence and activity of mechanisms particularly relevant to nanocrystalline materials. We will first focus on the atomic motion within grain boundaries in the elastic domain and then show some results in the case of plasticity.

5.4.1 Elastic Deformation: Molecular Simulations and the Structural Unit Model

Let us now show the advantage of the structural unit model in understanding particular behaviors of grain boundaries in the elastic regime. For this purpose several bicrystal interfaces where constructed via molecular statics (the construction method is described in Chapter 4). The following seven bicrystal interfaces were subjected to an increasing tensile load perpendicular to the grain boundary plane (see Table 5.2):

<table>
<thead>
<tr>
<th>Interface</th>
<th>Angle (°)</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Σ13(510)</td>
<td>22.6°</td>
<td>CDD</td>
</tr>
<tr>
<td>Σ17(410)</td>
<td>28.9°</td>
<td>CD.CD</td>
</tr>
<tr>
<td>Σ5(310)</td>
<td>36.9°</td>
<td>C</td>
</tr>
<tr>
<td>Σ29(730)</td>
<td>46.4°</td>
<td>B'B'C</td>
</tr>
<tr>
<td>Σ5(210)</td>
<td>53.1°</td>
<td>B'B'</td>
</tr>
<tr>
<td>Σ17(530)</td>
<td>61.9°</td>
<td>AB'</td>
</tr>
<tr>
<td>Σ13(320)</td>
<td>67.4°</td>
<td>AB'.AB'</td>
</tr>
</tbody>
</table>

Upon applying the increasing tensile load to the different bicrystal interfaces, their excess energies (with respect to the bulk energy) were recorded. The predicted excess energy evolutions for each interface are presented in Fig. 5.13(a). It can be seen that grain boundaries containing mixtures of only C and B' structural units present a decrease in their excess energies. Therefore, in the case studied, B' and C structural units appear to be less efficient at storing elastic energy than other structural units. However, as shown in Fig. 5.13(a), grain boundaries containing a mixture of B' or C structural units with either A or D structural units, which are basically perfect lattice regions, exhibit an increase in excess energy upon applying a tensile load on the bicrystal. Surrounded by A or D structural units, a B' or C structural unit is more likely to be able to expand in the lateral direction which would enhance the grain boundary ability for energy storage.

Also, one can notice in Fig. 5.13(a) the presence of sudden changes in the slope of the energy evolution of all grain boundaries containing C structural
units. The structure of a $\Sigma 13(320)$ AB’.AB’ and of a $\Sigma 13(510)$ CDD interface under 5 GPa tensile load are presented in Fig. 5.13(b) and (c). In Fig. 5.13(c) one can observe that the occurrence of an elastic transition mechanism which corresponds to the motion of atoms on each side of the grain boundary median plane. The excess energy of the grain boundary increases after the elastic transition has occurred. This mechanism may be a precursor to the grain boundary dislocation emission mechanism.

### 5.4.2 Plastic Deformation: Disclination Model and Dislocation Emission

Let us now present one of the many applications of disclination-based grain boundary models. For more detail the reader is referred to work by Gutkin [24, 25], Romanov [21], and others [26, 27]. The mechanism of dislocation
Fig. 5.14 Disclination-based model for grain boundary dislocation emission: (a) schematic [24] and (b) energy evolution as a function of emission distance $p$ for 4 different angle configurations: (1) $\phi_1 = \phi_2 = 45^\circ$, (2) $\phi_1 = 30^\circ$ and $\phi_2 = 45^\circ$, (3) $\phi_1 = 20^\circ$ and $\phi_2 = 30^\circ$, and (4) $\phi_1 = \phi_2 = 2^\circ$. 

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emission from grain boundaries has suggested particular interest in the NC community. While this mechanism is often studied via molecular simulations, disclination-based grain boundary representations are particularly suited to treat such problems for it has been shown that disclination motion is related to dislocation emission or absorption. Gutkin et al. [24] thus represent a grain boundary in a bicrystal as the concatenation of screened wedge disclinations of strength $\pm w = \pm (\theta_1 - \theta_2)$ (see Fig. 5.14(a)). Here, $\theta_1$ and $\theta_2$ represent two reference grain boundary misorientations. Note that the grain boundary representation used here is different from that of Li presented in previous section. In particular, the distance in between two disclinations of opposite sign is equivalent to an edge dislocation wall. It is assumed that the emission of two dislocations within each grain composing the bicrystal results from the motion of a wedge disclination of a distance $l$. It is thus suggested that grain boundary reorientation occurs as a result of grain boundary dislocation emission.

The mechanism of grain boundary dislocation emission by disclination motion is favorable if the energy after emission of the dislocation is lower than the system’s initial energy. The initial energy of the system is simply the sum of a wedge disclination dipole’s energy and of an edge dislocation wall. The energy after emission of a dislocation is the sum of the dipole’s energy, in its new configuration, the dislocation wall energy, the energy of each emitted dislocation, and their interaction energies.

Disregarding any activation energy contribution, which can be obtained solely with molecular simulations, it can be seen in Fig. 5.14(b) that, depending on the angle at which dislocation are emitted, the process may be favorable. For example, emission of two dislocations symmetrically at a 45° angle with respect to the grain boundary longitudinal axis is not predicted to be favorable while an asymmetric emission with 20° and 30° orientations for dislocation 1 and 2, respectively, is a favorable process.

5.5 Summary

This chapter introduces a simple description of grain boundary geometry. In particular, symmetric tilt and twist grain boundaries are described as well as their excess energy evolution with misorientation angle. The presence of energy cusps is noted and motivates the introduction of four different structure/energy correlation models.

The first model introduced is that of Read and Shockley, which is valid in the low misorientation range, and based on the representation of grain boundaries as arrays of one or more types of dislocations. The coincident site lattice model and the O-lattice theory are then introduced. The fundamental novelty in these models is that while they do not allow quantitative prediction of grain boundary energies, a geometrical description of the degree of fit between two adjacent grains in the grain boundary region is introduced. The model suggests that in the neighborhood of grain boundary cusp orientations, grain boundaries shall exhibit the presence of secondary dislocations in order to keep a structure close to the metastable configuration (e.g., energy cusps).
Finally, the structural unit model and the disclination model are introduced. The first model, which is an extension of Read and Shockley’s initial model, is based on the representation of grain boundaries as repeated sequences of particular atomic arrangements (structural units) whose energies are calculated by atomistic simulations. The disclination model, which is limited to predicting the excess energy between two non-necessary consecutive cusps orientations, is based on the existence of equivalent representations between dislocation arrangements and disclination arrangements, which is recalled as an introduction to disclination theory.

This chapter is concluded with two examples showing the use of molecular simulations, the CSL model and the disclination model, to investigate particular mechanisms associated with grain boundary–mediated deformation (e.g., elastic instabilities and grain boundary dislocation emission).

References

19. Li, J.C.M., Surface Science 31, (1972)